

COMPARISON OF PARTICLE-RESOLVED DIRECT NUMERICAL SIMULATION AND 1D MODELLING OF CATALYTIC REACTIONS IN A CYLINDRICAL PARTICLE BED

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Abstract. This work presents a comparative study of reactive flow in a realistically packed array of cylindrical particles on two widely different scales: particle-resolved direct numerical simulation (PR-DNS) and 1D modelling. PR-DNS directly simulates all transfer phenomena in and around the cylindrical particles, while 1D modelling utilizes closure models to predict system behaviour at a computational cost several orders of magnitude lower than PR-DNS.

PR-DNS is performed on a geometry of ~100 realistically packed cylindrical particles generated using the discrete element method (DEM). Simulations are performed over a range of Thiele moduli, Prandtl numbers and reaction enthalpies. The geometry with particles of aspect ratio four is meshed with fine polyhedral elements both inside and outside the particles. Hence, we obtain accurate results for combined internal and external heat and mass transfer in the cylindrical particle array.

These results are compared with a 1D packed bed reactor model incorporating appropriate models for intra particle diffusion and for external heat and mass transfer (applicable to cylindrical particles). Results document a good comparison for the heterogeneous first order

catalytic simple reaction. Therefore, recommendations are made to guide future 1D modelling works involving reactive flows in packed beds of cylindrical particles.

NOMENCLATURE

Greek Symbols

α	Volume fraction
ϵ	Void fraction
ϕ	Thiele modulus (Th)
η	Effectiveness factor

Latin Symbols

a	Characteristic length of cylinder particle ($r_p/2$)
C_p	Specific heat capacity of fluid [J/kg.K]
C_A	Concentration of species A [mol/m ³]
D	Molecular diffusivity [m ² /s]
d_p	Diameter of the cylindrical particle [m]
E	Activation energy [J/mol]
h	Heat transfer coefficient [W/m ² K]
k_0	Arrhenius constant [1/s]
K_f	Thermal Conductivity of fluid [W/m.K]
Nu	Nusselt number (hd_p/K_f)
Pr	Prandtl number ($\mu C_p/K_f$)
R	Gas constant [8.314 J/mol.K]
R_{cat}	Catalytic reaction rate [mol/m ³ s]
r	Radius [m]
Re	Reynolds number ($\rho u_s d_p/\mu$)
Sc	Schmidt number ($\mu/\rho D$)
Sh	Sherwood number (hd_p/D)
T	Temperature [K]
u_s	Superficial velocity of the fluid [m/s].

Sub/superscripts

f	Fluid
p	Particle.

1 INTRODUCTION

Cylindrical particles are often utilized in gas-solid packed bed systems, with application from process to pharmaceutical industry. Therefore, a wide range of closure models is available for gas-solid reaction systems. The closure models are segregated depending upon the application of the particles in either catalytic or non-catalytic role.

There are several important works describing the non-catalytic gas-solid systems [1, 2]. While, for the heterogeneous catalytic system the most important parameter of effectiveness factor is given for intra particle diffusion in spherical porous particle by [3]. The correct expression for the effectiveness factor with the cylindrical particle can be found in [4-6].

The recent work from the authors [7, 8] used the analytical expressions for effectiveness factor of general catalytic reaction forms in 1D packed bed models. The validity of these 1D packed bed models when combined with appropriate closure models for external heat and mass transfer in dense packed beds of cylindrical particle motivates the current work.

The objective of our work is to evaluate the predictions of gas-solid reaction systems on two distinct scales. Firstly, a PR-DNS on a geometry of ~ 100 densely packed cylindrical particles (aspect ratio four; $\varepsilon = 0.468$) [9] is used to give insight into the intra-particle diffusion and heat transfer phenomenon. Then the 1D packed bed model based on the closure for effectiveness factor [6] and external heat and mass transfer [9] is used to approximate this solution at a much lower computational cost. The comparison of the results for species concentration and temperature variation from both approaches are then documented.

2 METHODOLOGY

2.1 PR-DNS Simulation Setup

The realistically packed cylindrical particle bed of aspect ratio four ($\varepsilon = 0.468$) is generated using discrete element method (DEM) integrated in Star CCM+ 11.02. It is explained in more detail in Singhal et al. [9]. Such a geometry obtained is free from wall effects, which has been proved in [10]) hence giving confidence in the numerical accuracy of the methodology. The geometry is meshed with polyhedral elements with resolution $d_p/30$ using FLUENT meshing on particle surfaces both inside and outside the particle to account for intra particle diffusion. Subsequently a growth rate of 20% is allowed from the particle surface to fill up the void (Figure 1).

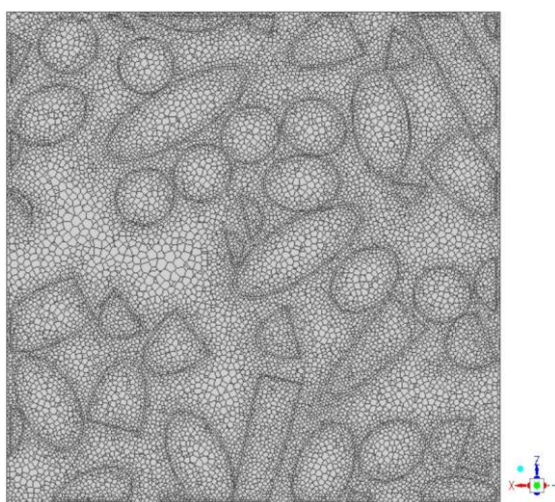


Figure 1: A section ($y = 0$) through the geometry of cylindrical particles meshed with polyhedral elements.

Steady state DNS with SIMPLE algorithm for pressure-velocity coupling and 2nd order spatial discretization for solver equations using ANSYS FLUENT is used to provide solution to the problem at hand. Steady state DNS is found to be accurate for the type of geometry solved, as transient fluctuations in the small spaces are negligible [10]. The final rendered geometry has a velocity inlet, pressure outlet and a non-slip condition on the wall. The solid particles are considered to be porous (the grain model [11]), where the reaction modelled by Eq. (1) takes place. Table 1 describes the simulation parameters used in the DNS.



The reaction rate is defined by Eq. (2) and (3):

$$R_{cat} = \alpha_s k C_A \quad (2)$$

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (3)$$

PR-DNS was performed for different combinations of heat transfer resistance (Prandtl number) and mass transfer resistance (Thiele modulus). In total, nine combinations of Thiele modulus and Prandtl number were used to obtain the results (Table 1). Different mass and heat transfer mechanisms are obtained by varying the molecular diffusivity and thermal conductivity of the gas phase using Thiele modulus (Th) and Prandtl number (Pr) definition given in Table 1. Using an appropriate pre-exponential factor (Eq. (3)), the value for reaction rate constant of 10000 1/s at temperature 1000 K is obtained. Similarly, a high value for activation energy is assumed to create a strong coupling between heat and mass transfer.

Table 1: Simulation parameters for PR-DNS

Parameters	Value
Eq. Particle diameter (d_e) (m)	0.001
Packed bed voidage	0.468
Particle void fraction (internal)	0.3
Density (kg/m^3)	Fluid :1 Particles :2500
Fluid velocity (m/s)	1
Inlet mole fraction (A)	0.1
Specific heat capacity (C_p) (J/kg/k)	1000
Arrhenius constant (k_0) (1/s)	1673603814
Activation energy (E) (J/mol)	100000
Thermal conductivity (Solid) (W/m.K)	0.1
Thiele moduli (Th)	5, 10, 20
Prandtl numbers (Pr)	0.50, 0.75, 1
Heat of reaction (kJ/mol)	100, 10, 0, -10

2.2 Thiele Modulus and Effectiveness Factor

The effectiveness factor and Thiele modulus [12] definition is similar to the previous work with spherical particle [8] defined for heterogeneous catalytic gas-solid reactions of first order. It is defined as the effect of intra particle diffusion on reaction rate [3, 13].

$$\eta = \frac{\text{actual reaction rate}}{\text{reaction rate without diffusion limitations}} \quad (4)$$

$$\phi \approx \frac{\text{reaction rate}}{\text{diffusion rate}} \quad (5)$$

2.3 1D Packed Bed Model

An outline of the 1D model setup can be seen in detail in the earlier work of the authors [7, 8]. The 1D packed bed model domain consists of 100 cells in one direction. The model is simulated using a Two Fluid Model approach in ANSYS FLUENT 17.2. The velocity of the solid phase in all 100 cells is fixed to zero. Subsequently, the conservation for mass, momentum, energy and specie are solved to obtain the solution.

In the 1D-model approach, appropriate closure models applicable to cylindrical particle beds have to be used to account for heat and mass transfer limitations. The closure models for effectiveness factor to model intra particle mass transfer limitations are given by Levenspiel [3], these closures are modified as suggested by [6], to be now applicable for cylindrical particles. Moreover, the external heat and mass transfer limitations are modelled using the closure models developed for cylindrical particles [9]. The effectiveness factor closures considered in this work are given below in Eq. (6)-(8):

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi} \right) \quad (6)$$

$$\phi = a \sqrt{\frac{k}{D_e}} \quad (7)$$

$$D_e = \frac{D\varepsilon}{\tau} \quad (8)$$

The Thiele modulus (ϕ) represents the ratio of kinetic rate to diffusion rate, so higher values represent greater mass transfer limitation. The effective diffusivity (D_e) is composed of the molecular diffusivity (D), the void fraction of porous particles ($\varepsilon = 0.3$) and the tortuosity ($\tau = 1$). The correlation for external heat (Pr) and mass transfer (Sc) from Singhal et al. [9] is written as shown in Eq. (9).

$$\begin{aligned} Nu &= (0.81 + 0.0652\varepsilon^{-3.55} Re^{0.644} Pr^{0.456}) \\ Sh &= (0.81 + 0.0652\varepsilon^{-3.55} Re^{0.644} Sc^{0.456}) \end{aligned} \quad (9)$$

The domain dimensions and the boundary conditions are identical to the PR-DNS simulations. In addition, the solid volume fraction is set as the mean volume fraction of the solid in the PR-DNS domain (0.532) times the solid volume fraction in the particles (0.7).

3 RESULTS AND DISCUSSIONS

3.1 Heat and Mass Transfer in Densely Packed Cylinders

PR-DNS is performed over a range of Thiele moduli (Th 5-20) and Prandtl numbers (Pr 0.5-1) for a densely packed bed of cylindrical particles of aspect ratio four ($\varepsilon = 0.468$). The results for typical variation of gas temperature and specie concentration (of specie A) for an

endothermic reaction (at $dH_{rxn} = 10$ kJ/mol) are shown in Figure 2 and Figure 3. Figure 2 shows temperature variation over Pr 0.50 to Pr 1 (top to bottom). As the gas thermal conductivity decreases, the particle temperature decreases (Pr 1 has colder particles than at Pr 0.50). This is due to increase in heat transfer resistance with increasing Prandtl number that limits the influx of heat consumed by the endothermic reaction. Also, for a fixed heat transfer resistance (Figure 2 (right to left)), a lower mass transfer resistance results in colder particles due to a faster endothermic reaction.

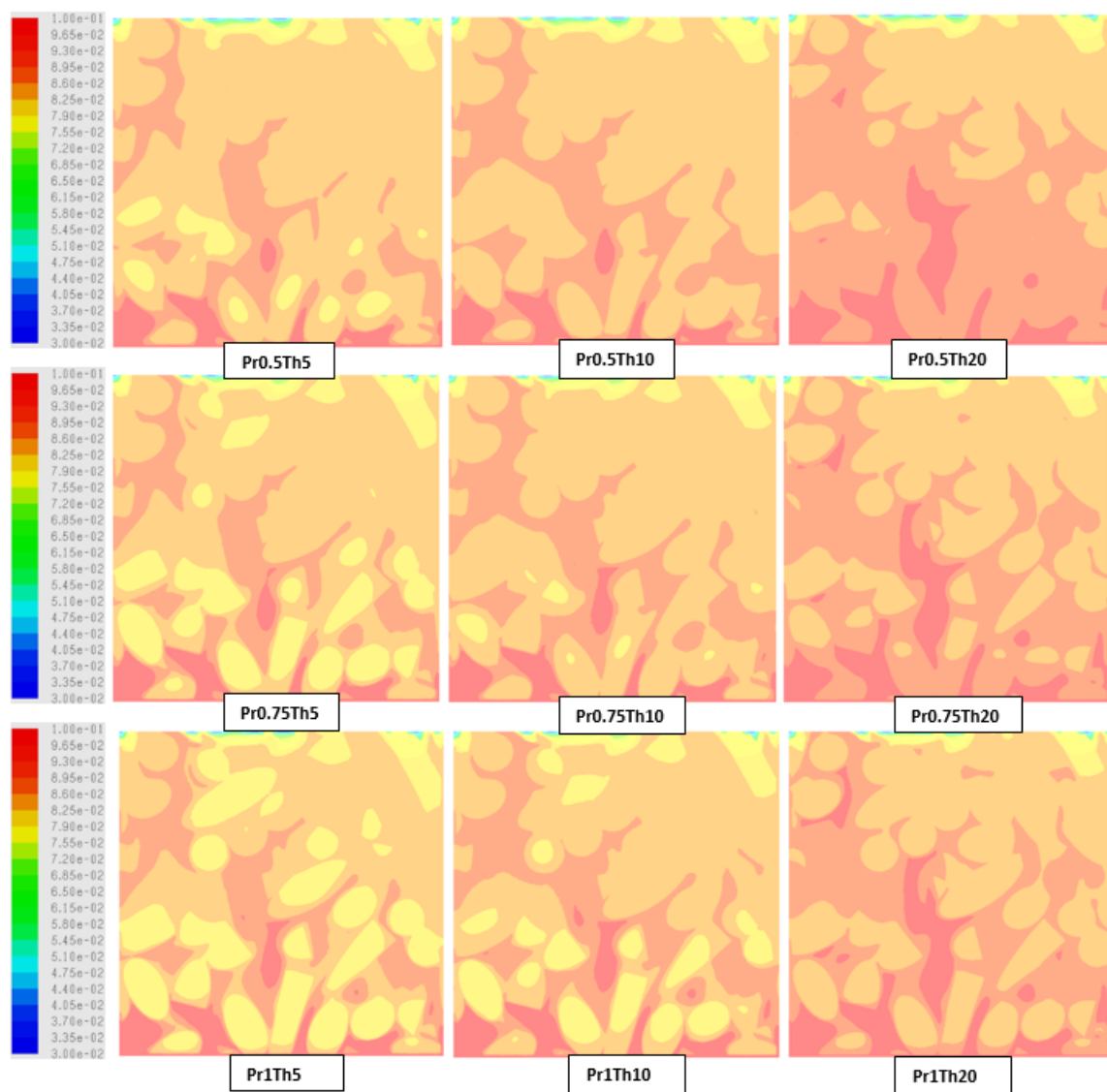


Figure 2: PR-DNS results (plane $y=0$) for the temperature variation in the packed bed of cylindrical particles of aspect ratio four for different Prandtl numbers (Pr) and Thiele moduli (Th) at $dH_{rxn} = 10$ KJ/mol.

The mass transfer limitations can be seen appropriately in Figure 3. It is evident from Figure 3 (left to right), that the concentration of specie A inside the particle decreases. This is because

of the increase in the mass transfer resistance, i.e. the gas mass diffusivity decreases with increase in Thiele modulus. More details are given in the subsequent sections.

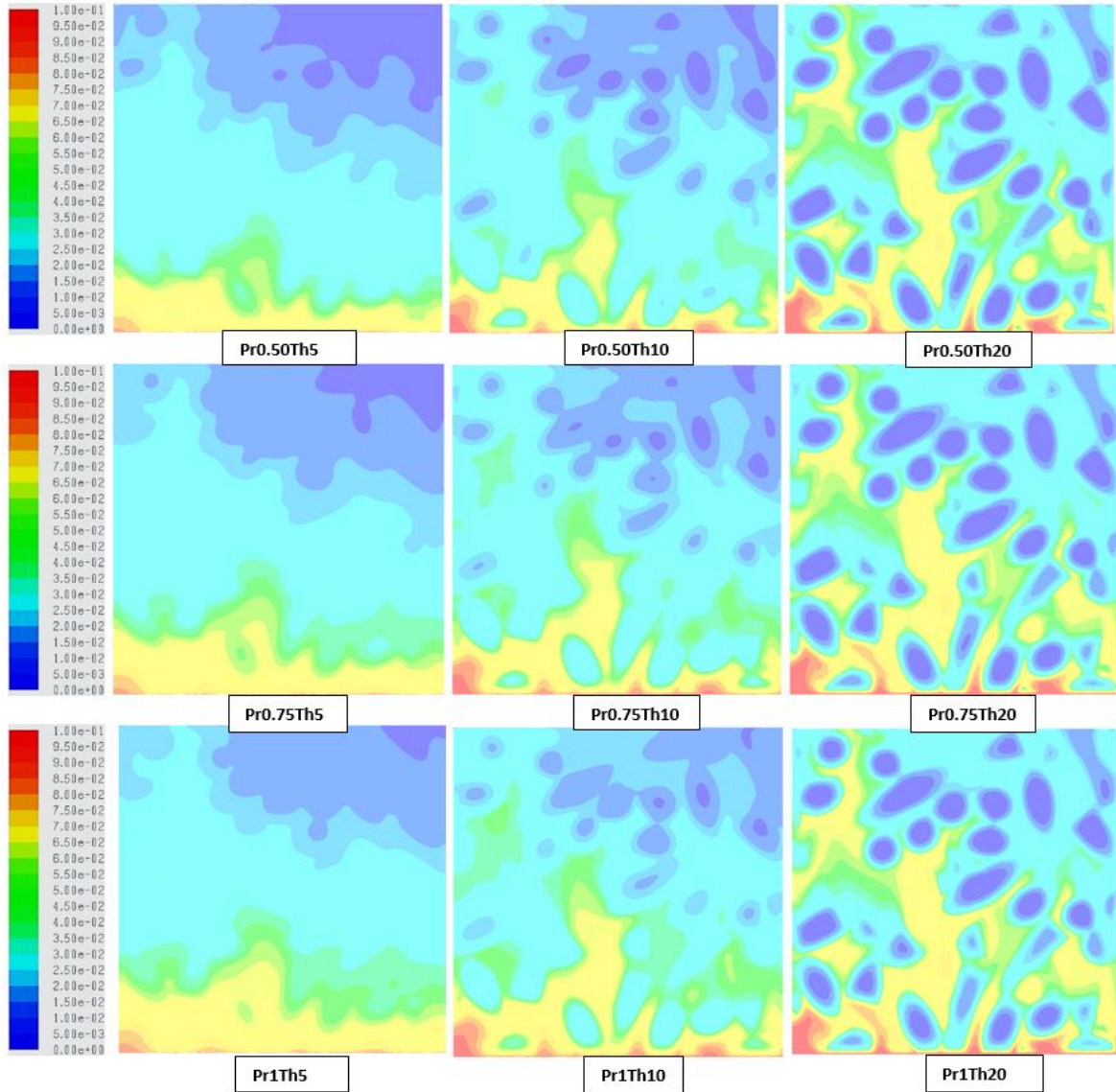


Figure 3: PR-DNS results for the reactant (A) mole fraction in the packed bed of cylindrical particles of aspect ratio four for different Prandtl numbers (Pr) and Thiele moduli (Th) at $dH_{rxn} = 10$ KJ/mol.

The effect of heat of reactions (dH_{rxn}) on specie concentration (of A) is shown in Figure 4. Four different dH_{rxn} ($= 100, 10, 0, -10$ kJ/mol) are assessed for the Pr1T20 case, including one exothermic reaction. The specie concentration (of specie A) inside the particle decreases as we decrease the dH_{rxn} . This is because an exothermic reaction is self-strengthening (faster reaction \rightarrow higher temperature \rightarrow faster reaction), whereas the opposite is true for an endothermic reaction. The exothermic reaction strengthens itself by increasing the temperature, while the endothermic reaction extinguishes itself by decreasing the temperature.

3.2 1D Model Predictions

The comparison between the PR-DNS data and the 1D model predictions are presented in this section. In the first comparison, the 1D model data is compared with the PR-DNS data for bulk fluid specie concentration and temperature (over a range of Prandtl number and Thiele modulus). The bulk fluid [9, 10, 14-16] properties are used for PR-DNS data to generalise any effect of the location of the planes [9, 10] in the geometry in the calculation of the temperature and specie concentration. Secondly, the effect of change in reaction enthalpies are compared. Also note that for the 1D model all the heat of reaction source term is implemented in the solid phase as suggested in our previous work [8].

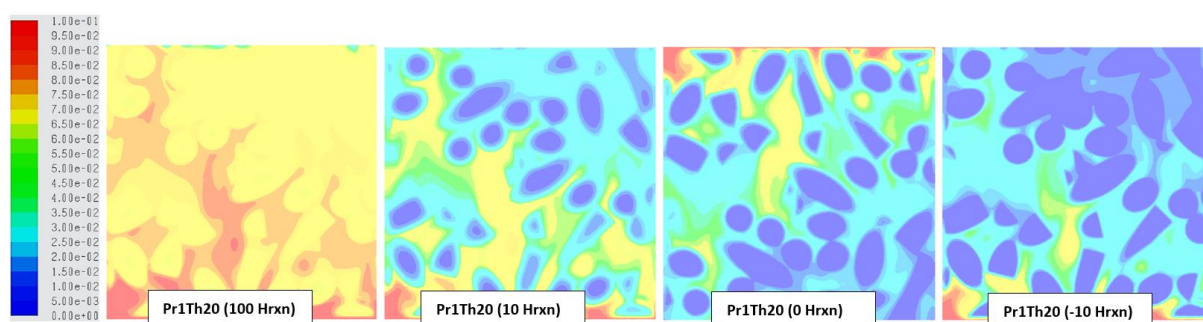


Figure 4: PR-DNS results for the reactant (A) mole fraction for ($Pr = 1$; $Th = 20$) case. The variation in specie concentration with different heat of reactions ($dH_{rxn} = 100, 10, 0, -10$) is shown from left to right.

3.2.1 Variation of Prandtl number and Thiele modulus

Figure 5 shows the axial specie concentration (for specie A) profiles for nine combinations of Thiele modulus and Prandtl number. The results agree well with the PR-DNS results suggesting that mass transfer limitations are defined with appropriate closures for 1D model. Figure 6 shows the axial profiles for the difference between the bulk gas temperature and the average particle temperature. The amount of reaction in an endothermic system decreases as Pr is increased by decreasing the gas phase thermal conductivity. A lower thermal conductivity implies greater gas-particle heat transfer resistance, thereby allowing less heat to enter and sustain the highly endothermic reaction. The temperature variation inside each particle should be very small given the solids phase thermal conductivity (Table 1) implemented. In general, good agreement between PR-DNS and 1D results is obtained with a moderate discrepancy at $Pr = 1$.

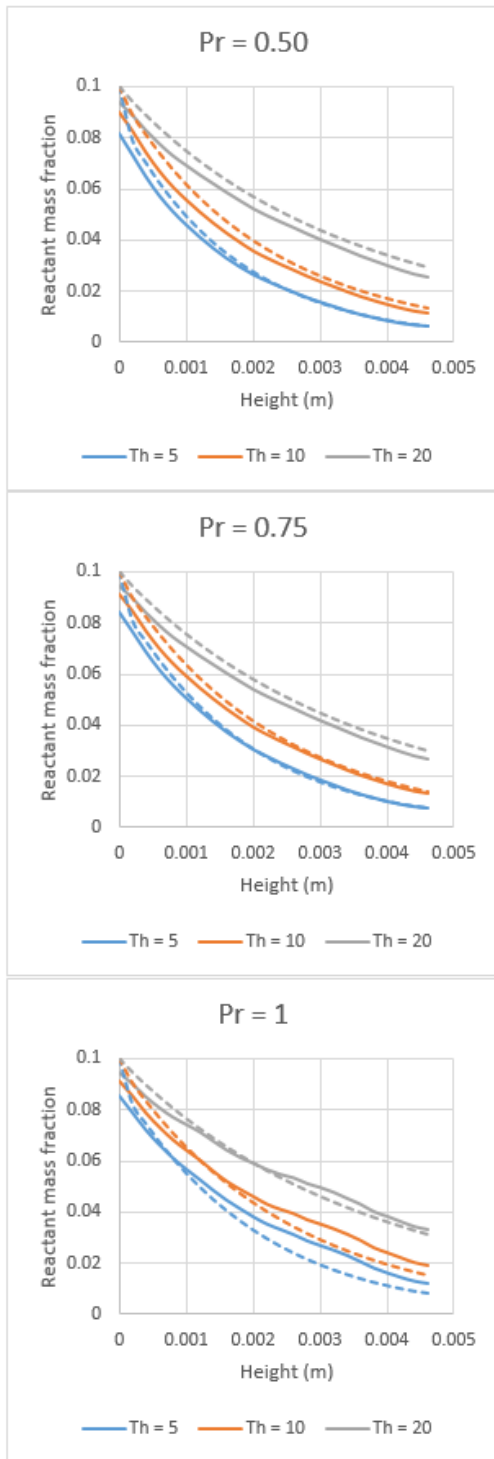


Figure 5: Comparison of axial species profiles (for specie A) between PR-DNS (solid lines) and 1D simulations (dashed lines) for different Prandtl numbers (Pr) and Thiele moduli (Th) at $dH_{rxn} = 10$ kJ/mol..

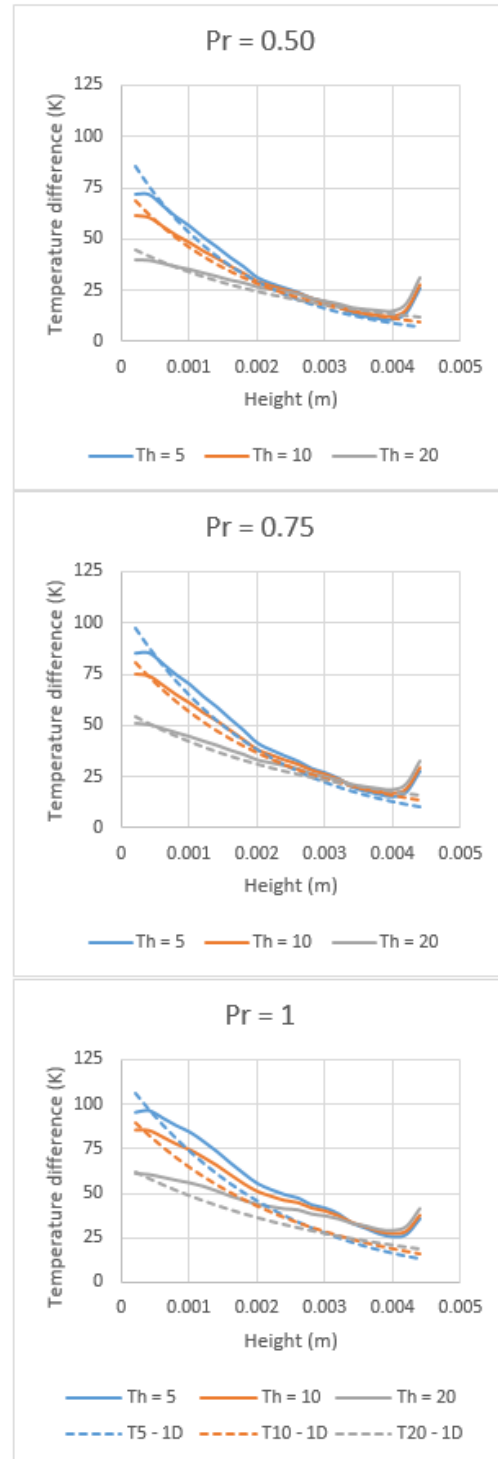


Figure 6: Comparison of axial gas-particle temperature difference between PR-DNS (solid lines) and 1D simulations (dashed lines) for different Prandtl numbers (Pr) and Thiele moduli (Th) at $dH_{rxn} = 10$ kJ/mol.

3.2.2 Variation of reaction enthalpy

In the previous sections, the heat of reactions used is ($dH_{rxn} = 10$ kJ/mol) signifying an endothermic reaction. In order to monitor the effect of dH_{rxn} on the reactant conversion, three additional heat of reactions (including an exothermic reaction) are evaluated for the case (Pr1T20) with greatest heat and mass transfer limitations.

It can be seen from Figure 7 that the 1D model predicts PR-DNS results accurately and the reactant conversion increases with a decrease in the reaction enthalpies. In the two cases with the fastest reaction rates, the inclusion of the external mass transfer limitation becomes important to achieve a good match with PR-DNS results.

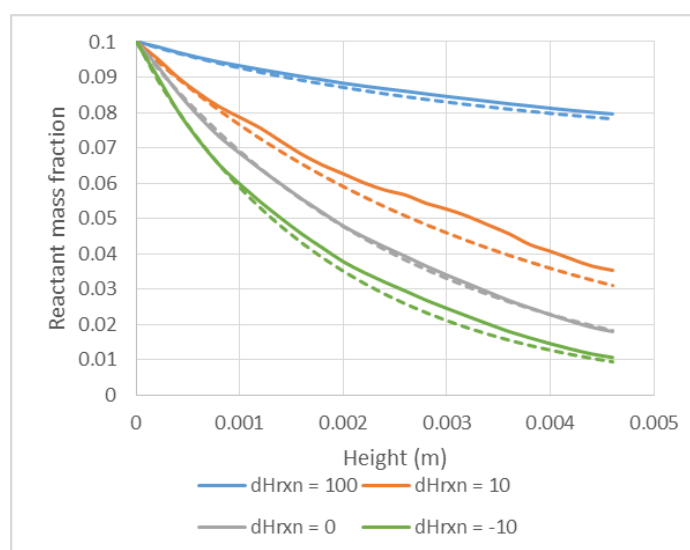


Figure 7: Comparison of axial species profiles (for specie A) between PR-DNS (solid lines) and 1D simulations (dashed lines) for Pr1T20 case and different reaction enthalpies (dH_{rxn} in kJ/mol).

11 CONCLUSIONS

This work presented a comparison of particle-resolved direct numerical simulations (PR-DNS) with 1D packed bed model for a densely packed bed of cylindrical particles of aspect ratio four ($\epsilon = 0.468$) in a gas-solid first order catalytic reaction system.

Existing closures for 1D packed bed model for spherical particles modified appropriately for cylindrical particles predicts well against the result for resolved simulations (PR-DNS) over a range of Thiele moduli, Prandtl numbers and reaction enthalpies. Recently proposed closures for external heat and mass transfer from cylindrical particles were important to ensure good performance of the 1D model. Future works will assess whether this good performance is maintained in systems with multiple reactions with different reaction orders.

12 ACKNOWLEDGEMENT

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